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(54) Title: POROUS MATERIALS AND METHOD FOR PRODUCING

(57) Abstract

An improved method for producing porous materials is provided comprising the steps of preparing a slurry comprising a binder and metal powder, impregnating a foam structure of organic material, curing the impregnated slurry within the foam structure, burning off the foam structure, decarburizing the resulting structure and sintering the resulting porous material product in vacuum. The sintering and decarburizing steps may be performed in a partial pressure atmosphere of reactive gas which will not adversely react with the porous metal product.

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DESCRIPTION

POROUS MATERIALS AND METHOD FOR PRODUCING

Technical Field

This invention relates to a method of producing porous materials and structures therefrom. More particularly, this invention relates to improvements in the production of porous materials, said improvement providing porous materials previously unavailable in the art and providing porous materials previously available in the art, but having improved quality and properties.

Background Art

It is well known in the art that porous materials, also know as foam materials, are capable of production by various methods. The porous materials produced in the art are in the family of ceramics, porous metals and porous metal compounds.

The porous or foam materials, hereinafter referred to as porous materials, comprise an aggregation of closed cells resulting in a density of the porous material being less than that of the solid material. The porous materials best developed are generally free of directionality and have significant structural strength.

The prior art teaches the use of various methods for the production of porous materials. Porous metals having a plurality of randomly disbursed closed cells throughout a metal matrix are generally prepared by using a heat decomposable firming agent to generate the gas to form the cells.

The prior art teaches the use of various methods for the production of both ceramic and metallic porous materials.

Ball - U.S. Patent No. 3,111,396, teaches the method of making a porous material comprising the steps of impregnating a porous organic structure with a suspension of a powered material in a fluid, slowing drying the impregnated organic structure, heating the impregnated organic structure to decompose the organic structure and the fluid while closely

retaining the shape and size of the original organic structure, and then heating the impregnated carbon-powered material structure to further join the powder into a continuous form. Ball teaches the use of an inert atmosphere for refractory metals to complete the required heating steps and a reducing atmosphere in most other cases.

Other prior art relating to the development of foamable metal products include *Worz, et al.*, - U.S. Patent No. 5,393,485 wherein a metal powder is mixed with a foaming agent powder and the subsequent mixture brought to an elevated temperature in a receiver and then extruded through a dye and the extruded parts subsequently foamed by decomposition of the foaming agent by heating. *Kenney, et al.*, U.S. Patent No. 5,281,251 provides a method for producing metal foam by discharging gas bubbles into a molten metal composite to form a foam.

Baumeister, et al. - U.S. Patent No. 5,151,246 discloses a method for producing a foam metal body utilizing a gas-splitting propellant powder.

Ginn, et al. - U.S. Patent No. 4,973,385 describes a method for producing foam metal through the introduction of gaseous bubbles within a mass of molten metal during foaming. A second patent by *Ginn, et al.* - U.S. Patent No. 5,112,697 further describes a method for producing foam metal in which gaseous bubbles are retained within a mass of molten metal during foaming. Additional methods disclosing the formation of foamed metal products are shown by *Akiyama, et al.* - U.S. Patent No. 4,713, 277 and U.S. Patent No. 4,099,961 and *Niebylski, et al.* - U.S. Patent No. 3,794,481 and *Rock* - U.S. Patent No. 3,782,919 and *Rock* - U.S. Patent No. 3,773,098, and *Valdo* - U.S. Patent No. 3,756,303 and *Bjorksten, et al.* - U.S. Patent No. 3,707,367 and *Barry, Jr., et al.* - U.S. Patent No. 3,705,303, *Hall* - U.S. Patent No. 3,692,513, *Barry* - U.S. 3,671,221, *Mouwen* - U.S. Patent No. 2,979,400, *Elliot* - U.S. Patent No. 2,751,289 and *Niebylski* - U.S. Patent No. 3,940,262 which provides a foam metal article having reinforcing fibers therein.

Additionally, the prior art provides for the method of producing ceramic composite foams such as, *Park, et al.* - U.S. Patent No. 5,296,416, *Park, et al.* - U.S. Patent No. 5,185,297, *Kaettlitz, et al.* - U.S. Patent No. 5,169,542, *Narumiya* - U.S. Patent No. 4,302,502, *Dore, et al.* - U.S. Patent No. 4,024,212, *Kesten, et al.* - U.S. Patent No. 3,451,841, *Holland* - U.S. Patent No. 3,097,930, *Schwartzwalder, et al.* - U.S. Patent No. 3,090,094, *Fujii, et al.* - U.S Patent No. 2,921,357, and *Bellamy* - U.S. Patent No. 1,938,170.

None of the prior art methods described include the advantages inherent in the instant invention. The prior art fails to teach the development of various porous materials using heating in vacuum. The prior art further fails to teach the application of metal powder to a reticulated organic precursor material using a dry powder coating technique not requiring the use of a powder suspension slurry.

In addition, the method described herein is adaptable to a wide range of materials not previously available, and is suited to easy production of products in a variety of materials, sizes, shapes and cell densities.

DISCLOSURE OF INVENTION

A primary objective of the present invention is to provide a new and novel method for producing porous metals.

A second object of the present invention is to provide porous metals, previously unavailable, having a high level and repeatability of quality.

Another object of the present invention is to provide a method for producing porous metals in a reduced number of steps as required by the prior art.

Yet another object of the present invention is to provide a method for producing porous metals with controlled pore size.

A further object of the present invention is to provide a method for producing porous metals using binders with little or no carbon residue.

Another object of the present invention is to provide a method of dry powder application to an organic precursor material that does not require the use of a binder-powder slurry.

A still further object of the present invention is to provide a method for producing porous metals utilizing vacuum techniques.

These and other objects, features and advantages of the invention will be more fully understood from the following detailed description, taken in conjunction with the accompanying drawings and examples, all of which are intended to be typical of, rather than in any way limiting on the scope of the present invention.

The prior art teaches the development of porous metal structures utilizing binders having a high carbon content, drying the sample slowly, heating the sample to a temperature capable of volatilizing the binder and foam but not destroying the structure, heating the structure to a second temperature to weakly bond the carbon-metal powder structure and heating the sample to a third temperature to sinter. The prior art teaches the use of steam to be added to Hydrogen to reduce the amount of carbon present to give a strong final product. The prior art work utilizes heating in a retort. Ball teaches that the mechanical step of sintering the metal or further joining of other powders to produce a foamed product may not be effectively utilized in the production of certain porous materials such as columbium because of their affinity for carbon presenting the possibility of forming carbides which can be undesirable.

It is to be understood by one skilled in the art that the presence of oxides in certain porous material would also be deleterious to the porous product.

To overcome the prior art problems, the present invention provides a method of producing a wide range of porous materials, particularly metals and metal compounds capable of producing porous metals with properties equal to the base or elemental metal.

The present invention provides a method of producing porous materials which eliminates the preparation and use of a binder-metal powder slurry required by the practice of the prior art.

Briefly, one form of the present invention provides a method for producing a porous material including the steps of preparing a slurry comprising a binder and metal powder, impregnating a foam structure or organic material, curing the impregnated slurry with the foam structure, burning off the foam structure, decarburizing the resulting structure and sintering the resulting porous material product in vacuum. The improved method of the present invention offers uses not previously available in the art.

BRIEF DESCRIPTION OF DRAWINGS

For a better understanding of the present invention, reference may be had to the following descriptions, taken in conjunction with the accompanying drawings wherein:

Fig. 1 is a flow chart of the method of making porous material, utilized in the present invention.

Fig. 2 is a flow chart of an alternate method of making porous material, utilized in the present invention.

Fig. 3 is a sectional view of a porous material structure developed by application of the present invention.

BEST METHOD FOR CARRYING OUT THE INVENTION

The present invention overcomes the deficiencies previously discussed in the prior art and provides a method for producing porous metals which are fully sintered open cell reticulated foam-like structures. A typical resulting open cell porous metal developed by the method of the present invention is shown in **Fig. 3**. The present invention starts with a reticulated interconnected web precursor to which a slurry of binder and metal coating is applied or to which metal powder is applied by other

means. A thermal cycle or cycles is applied during which the precursor is removed and the coating sintered leaving a rigid structure. Part or all of the thermal cycles are to be conducted in a vacuum to overcome the prior art limitations.

The porous metal foam thus produced is 2% to 20% dense (98% to 80% porous) and is extremely lightweight. The resultant porous metal product has a very high surface area when compared to that of a same sized, non porous shape. Approximately a 1500 times or greater surface area is provided.

The following examples are given as illustrative of the method of the present invention for preparing porous materials and are exemplary of the wide variety of modifications and variations of which the invention is capable. The examples are meant to be illustrations of, rather than limitations, on the scope of the present invention which is defined in the appended claims.

EXAMPLE 1

Copper porous material is produced using the general steps shown in **Fig. 1**. Initial steps include preparing a slurry of binder and elemental powder mixed in a 2-4 parts binder to 6-8 parts copper oxide or copper powder mixture. Current binder systems for copper porous materials include a phenolic binder from Borden and a PVA (poly vinyl acetate) binder from H.B. Fuller. It is to be understood by one skilled in the art that other binder systems are capable of use if the proper curing cycles are

used. Mixing of the slurry may be done by hand, electric mixing device or a ball mill may be used.

The slurry is next impregnated into the pores of a selected reticulated foam material with an interconnecting web of structural material and void spaces. The pore size of the selected foam material is selected based upon the desired pore size of the final porous material product. The slurry is introduced into the pores of the selected foam material and the excess is removed by hand, rollers or other method until only the webbing of the foam material is coated. It is to be understood by one skilled in the art that the foam material can also be impregnated without the use of a slurry mixture by coating the foam with binder and sprinkling or spraying the copper powder on the webs or by application using a fluidized bed. This process is repeated to achieve the web thickness or density desired. The foam material can also be impregnated with a mixture of binder and powder using an air brush or paint gun apparatus. This slurry requires more binder than the hand impregnation slurry when this procedure is used.

The impregnated foam structure is cured in air to set the binders (either phenolic or PVA) at 250 to 350 Degrees F for 0.5 to 3 hours.

The foam structure is heated from room temperature to 1200 - 1600 Degrees F in 2 - 3 hours in 20 -30 scfh of any inert or reducing atmosphere to burn off the reticulated foam material. The foam structure can alternatively be burned off by heating in an air furnace at 1700 Degrees F to 1900 Degrees F.

The parts are then decarburized by processing water through a retort at 0.5 to 1.0 gallons/hr. at 1200 - 1600 Degrees F. The time that the water is running depends on the amount of material present. Five (5) hours will decarburize approximately six (6) sheets of copper 12x12x0.5 inches. The porous metal parts can alternatively be decarburized by heating them in an air furnace from 1100 to 1900 Degrees F for 1 to 3 hours.

The porous metal parts are then sintered at 1550 to 1800 Degrees F for 0.5 to 1.0 hrs. in Hydrogen.

EXAMPLE 2

Nickel porous material is produced using the general steps shown in **Fig. 1**. Initial steps include preparing a slurry of binder and elemental powder mixed in a 2-4 parts binder to 6-8 parts nickel oxide or nickel powder mixture. Current binder systems for nickel porous materials include a phenolic binder from Borden and a PVA (poly vinyl acetate) binder from H.B. Fuller. It is to be understood by one skilled in the art that other binder systems are capable of use if the proper curing cycles are used. Mixing of the slurry may be done by hand, electric mixing device or a ball mill may be used.

The slurry is next impregnated into the pores of a selected reticulated foam material with an interconnecting web of structural material and void spaces. The pore size of the selected foam material is selected based upon the desired pore size of the final porous material product. The slurry is introduced into the pores of the selected foam

material and the excess is removed by hand, rollers or other method until only the webbing of the foam material is coated. It is to be understood by one skilled in the art that the foam material can also be impregnated without the use of a slurry mixture by coating the foam with binder and sprinkling or spraying the nickel powder on the webs or by application using a fluidized bed. This process is repeated to achieve the web thickness or density desired. The foam material can also be impregnated with a mixture of binder and powder using an air brush or paint gun apparatus. This slurry requires more binder than the hand impregnation slurry when this procedure is used.

The impregnated foam structure is cured in air to set the binders (either phenolic or PVA) at 250 to 350 Degrees F for 0.5 to 3 hours.

The foam structure is heated from room temperature to 1200 - 1600 Degrees F in 2 - 3 hours in 20 -30 scfh of any inert or reducing atmosphere to burn off the reticulated foam material. The foam structure can alternatively be burned off by heating in an air furnace at 1700 Degrees F to 1900 Degrees F.

The parts are then decarburized by processing water through a retort at 0.5 to 1.0 gallons/hr. at 1200 - 1600 Degrees F. The time that the water is running depends on the amount of material present. Five (5) hours will decarburize approximately six (6) sheets of nickel 12x12x0.5 inches. The porous metal parts can alternatively be decarburized by heating them in an air furnace from 1100 to 2800 Degrees F for 1 to 3 hours.

The porous metal parts are then sintered at 1800 to 2300 Degrees F for 0.5 to 1.0 hrs. in Hydrogen.

It is to be understood that if the reticulated foam material is burned off using the alternate method presented above by heating at 1700 Degrees F to 1900 Degrees F a decarburization cycle will not be required.

It is to be understood that porous metallic material from the group of nickel, cobalt and iron may be formed using the method of Example 2.

EXAMPLE 3

High chromium containing nickel, nickel alloys and iron alloy porous material is produced using the general steps shown in **Fig. 2.** Initial steps include preparing a slurry of binder and elemental powder mixed in a 2-4 parts binder to 6-8 parts nickel oxide or nickel powder mixture. Current binder systems for most stainless steel porous materials include PVA (poly vinyl acetate) binder from H.B. Fuller. It is to be understood by one skilled in the art that other binder systems such as low carbon acrylics are capable of use if the proper curing cycles are used, as well as higher carbon binders such as phenolics, depending on the porous metal alloy to be produced. Mixing of the slurry may be done by hand, electric mixing device or a ball mill may be used.

The slurry is next impregnated into the pores of a selected reticulated foam material with an interconnecting web of structural material and void spaces. The pore size of the selected foam material is selected based upon the desired pore size of the final porous material product. The slurry is introduced into the pores of the selected foam

material and the excess is removed by hand, rollers or other method until only the webbing of the foam material is coated. It is to be understood by one skilled in the art that the foam material can also be impregnated without the use of a slurry mixture by coating the foam with binder and sprinkling or spraying the iron or nickel based powder on the webs or by application using a fluidized bed. This process is repeated to achieve the web thickness or density desired.

The foam material can also be impregnated with a mixture of binder and powder using an air brush or paint gun apparatus. This slurry requires more binder than the hand impregnation slurry when this procedure is used.

The impregnated foam structure is cured in air to set the binders (either phenolic or PVA) at 250 to 350 Degrees F for 0.5 to 3 hours.

The foam structure of the current example is easily oxidized at elevated temperatures if heated in air or reducing atmospheres at the temperatures required to burn off the organic foam precursor material. The cured foam structure is then heated to 1600 Degrees F to 2000 Degrees F in vacuum, nitrogen or an inert gas. If vacuum is used it should be a partial pressure of argon of 2500 to 3500 microns. The heating cycle discussed herein can alternatively be performed in a retort furnace at a gas level of 20 to 30 scfh of nitrogen or argon. The preferred method will utilize vacuum heating. Previous consideration of the industry shunned this step for fear of significantly reducing the life of the vacuum

diffusion pump. It is to be understood that hydrogen atmospheres are not to be used for this example.

The parts are then decarburized by heating in vacuum at 900 - 1200 Degrees F for 3 - 12 hours depending upon quantity of material. The resultant product will have extremely low carbon content (less than 0.1%) and will result in significant high temperature corrosion resistance of this class of alloys.

The porous metal parts are then sintered at 2200 to 2500 Degrees F for 0.5 to 1.0 hrs. in vacuum with partial pressure of Argon as previously discussed.

EXAMPLE 4

Alpha 4® (Registered Trademark of Alleghny Ludlum) porous metal, with a nominal chemistry of .015 C, .34 Mn, .014 P, .0001 S, 20.9 Cr., .15 Ni, 5.03 Al, .003 Cb, .0065 Ti, .014 N, .004 Mg, .014 Ce, and .006 La, is produced using the general steps shown in **Fig. 2**. Initial steps include preparing a slurry of binder and elemental powder mixed in a 2-4 parts binder to 6-8 parts Alpha 4® powder mixture. Current binder systems for most Alpha 4® porous materials include PVA (poly vinyl acetate) binder from H.B. Fuller. It is to be understood by one skilled in the art that other binder systems such as low carbon acrylics are capable of use if the proper curing cycles are used. Mixing of the slurry may be done by hand, electric mixing device or a ball mill may be used.

The Alpha 4® slurry is next impregnated into the pores of a selected reticulated foam material with an interconnecting web of structural

material and void spaces. The pore size of the selected foam material is selected based upon the desired pore size of the final porous material product. The slurry is introduced into the pores of the selected foam material and the excess is removed by hand, rollers or other method until only the webbing of the foam material is coated. It is to be understood by one skilled in the art that the foam material can also be impregnated without the use of a slurry mixture by coating the foam with binder and sprinkling or spraying the Alpha 4® powder on the webs or by application using a fluidized bed. This process is repeated to achieve the web thickness or density desired. The foam material can also be impregnated with a mixture of binder and powder using an air brush or paint gun apparatus. This slurry requires more binder than the hand impregnation slurry when this procedure is used. This process is best accomplished on pore sizes generating 50 ppi (pores per linear inch) or larger.

The impregnated foam structure is cured in air to set the binder selected at 250 to 350 Degrees F for 0.5 to 3 hours.

The Alpha 4® material of the current example contains elements that form stable oxides which cannot be reduced by hydrogen at any temperature. In order to sinter these materials elements such as chromium and aluminum must remain metallic. A vacuum furnace allows heating of these materials without formation of such oxides. The vacuum furnace further results in a quick and repeatable operation.

The cured foam structure is placed in a vacuum furnace, the chamber evacuated and the structure heated in vacuum to 2300 Degrees F

to 2450 Degrees F for 0.5 to 2.0 hrs. This operation is performed in a partial pressure of approximately 2500 to 3500 microns of Nitrogen or Argon to prevent vaporization of certain volatile elements such as chromium and the like and to further reduce wear of the vacuum diffusion pump. Previous consideration of the industry shunned this step for fear of significantly reducing the life of the vacuum diffusion pump. It is to be understood that hydrogen atmospheres are not to be used for this example.

It is to be further understood that porous metallic materials from the group comprising aluminum in solution, chromium, columbium, iron aluminides, nickel aluminides, materials containing rare earths in solution, and titanium aluminides may be produced using the method of Example 4.

EXAMPLE 5

Titanium and Titanium alloy porous material is produced using the general steps shown in **Fig. 2**. Initial steps include preparing a slurry of binder and elemental powder mixed in a 5-8 parts binder to 7-10 parts Titanium powder mixture. Current binder systems for most Titanium alloy materials include PVA (poly vinyl acetate) binder from H.B. Fuller. It is to be understood by one skilled in the art that other binder systems such as low carbon acrylics are capable of use if the proper curing cycles are used. Mixing of the slurry may be done by hand, electric mixing device or a ball mill may be used.

The slurry is next impregnated into the pores of a selected reticulated foam material with an interconnecting web of structural material and void spaces. The pore size of the selected foam material is selected based upon the desired pore size of the final porous material product. The slurry is introduced into the pores of the selected foam material and the excess is removed by hand, rollers or other method until only the webbing of the foam material is coated. It is to be understood by one skilled in the art that the foam material can also be impregnated without the use of a slurry mixture by coating the foam with binder and sprinkling or spraying the Titanium powder on the webs or by application using a fluidized bed. This process is repeated to achieve the web thickness or density desired. This is best accomplished on pore sizes of 50 ppi (pores per linear inch) or larger. The foam material can also be impregnated with a mixture of binder and powder using an air brush or paint gun apparatus. This slurry requires more binder than the hand impregnation slurry when this procedure is used.

The impregnated foam structure is cured in air to set the binders at 250 to 350 Degrees F for 0.5 to 3 hours.

The foam structure of the current example is highly reactive at elevated temperatures if heated in air or reducing atmospheres at the temperatures required to burn off the organic foam structure. The cured foam structure is placed in a vacuum furnace, the chamber evacuated and the structure heated in vacuum. This operation is performed in a partial pressure of approximately 2500 - 3500 microns of Argon to prevent

vaporization of certain volatile elements such as aluminum and the like and to further reduce wear of the vacuum diffusion pump. It is to be understood that Nitrogen and Hydrogen atmospheres are not to be used with Titanium products as same will adversely react with the Titanium products resulting in undesirable properties.

The porous metal parts are then sintered at 2200 to 2700 Degrees F for 0.5 to 1.0 hrs. in vacuum or partial pressure.

If extremely low carbon content is desired the sintered Titanium porous metal product can be decarburized by heating in air at 900 - 1100 Degrees F for 3 - 12 hours depending on the amount of material to be decarburized. An oxide layer will be formed on the porous metal which can be removed by treating in a dilute mixture of HF and HNO3. A layer of clean Titanium powder is placed on the porous metal product by the sprinkling technique or by spraying binder and powder to the structure and resintered in vacuum or partial pressure at a temperature of 2200 - 2700 Degrees F.

EXAMPLE 6

Metals and alloys comprising the group of precious metals including gold, silver, platinum, palladium and rhodium may be produced as follows. Platinum porous material is produced using the general steps shown in **Fig. 1**. Initial steps include preparing a slurry of binder and elemental powder mixed in a 2-4 parts binder to 6-8 parts platinum powder mixture. Current binder systems for Platinum porous materials include PVA (poly vinyl acetate) binder from H.B. Fuller. It is to be

understood by one skilled in the art that other binder systems such as low carbon acrylics are capable of use if the proper curing cycles are used. Mixing of the slurry may be done by hand, electric mixing device or a ball mill may be used.

The slurry is next impregnated into the pores of a selected reticulated foam material with an interconnecting web of structural material and void spaces. The pore size of the selected foam material is selected based upon the desired pore size of the final porous material product. The slurry is introduced into the pores of the selected foam material and the excess is removed by hand, rollers or other method until only the webbing of the foam material is coated. It is to be understood by one skilled in the art that the foam material can also be impregnated without the use of a slurry mixture by coating the foam with binder and sprinkling or spraying the Platinum powder on the webs or by application using a fluidized bed. This process is repeated to achieve the web thickness or density desired. This is best accomplished on pore sizes of 50 ppi (pores per linear inch) or larger. The foam material can also be impregnated with a mixture of binder and powder using an air brush or paint gun apparatus. This slurry requires more binder than the hand impregnation slurry when this procedure is used.

The impregnated foam structure is sintered in air at 2700 Degrees F to 3000 Degrees F for 0.5 to 2 hours. It is to be understood that unlike the previous examples, the precious metals will be treated in a single sintering cycle after the reticulated precursor foam is impregnated with the

binder and metal powder using either the slurry or the dry powder method of powder application. The variation to the general steps shown in **Fig. 1** relates to the single sintering step described herein.

EXAMPLE 7

Metals and alloys comprising the group of molybdenum, tantalum, columbium and tungsten metals may be produced as follows. Molybdenum porous material is produced using a combination of the general steps shown in **Figs. 1 and 2**. Initial steps include preparing a slurry of binder and elemental powder mixed in a 2-4 parts binder to 6-8 parts molybdenum powder mixture. Current binder systems for molybdenum porous materials include a phenolic binder from Borden and a PVA (poly vinyl acetate) binder from H.B. Fuller. It is to be understood by one skilled in the art that other binder systems such as low carbon acrylics are capable of use if the proper curing cycles are used. Mixing of the slurry may be done by hand, electric mixing device or a ball mill may be used.

The slurry is next impregnated into the pores of a selected reticulated foam material with an interconnecting web of structural material and void spaces. The pore size of the selected foam material is selected based upon the desired pore size of the final porous material product. The slurry is introduced into the pores of the selected foam material and the excess is removed by hand, rollers or other method until only the webbing of the foam material is coated. It is to be understood by one skilled in the art that the foam material can also be impregnated

without the use of a slurry mixture by coating the foam with binder and sprinkling or spraying the molybdenum powder on the webs or by application using a fluidized bed. This process is repeated to achieve the web thickness or density desired. The foam material can also be impregnated with a mixture of binder and powder using an air brush or paint gun apparatus. This slurry requires more binder than the hand impregnation slurry when this procedure is used.

The impregnated foam structure is heated to 1600 Degrees F to 2000 Degrees F in nitrogen to accomplish burn off of the organic reticulated precursor material. The material is next decarburized by holding at 1600 Degrees F to 2000 Degrees F in an atmosphere of 20 to 30 scfh of hydrogen with 0.1 to 0.25 gallons per hour of $H2O$ for a period of 6 to 10 hours. The material is then heated in a vacuum furnace to 2800 Degrees F to 3200 Degrees F for 0.5 to 2 hours.

It is to be understood that metals and alloys comprising the group tungsten, tantalum, molybdenum or other refractory alloys may be produced using the method of Example 7.

The present invention has application to the following pure metals and/or alloys containing these metals in the production of porous metal products therefrom: Chromium, Cobalt, Columbium, Copper, Iron Aluminides, Nickel, Nickel Aluminides, Molybdenum, Precious Metals of the group Gold, Silver, Platinum. Palladium, Rhodium, etc., Titanium, Titanium Aluminides, Tantalum and Tungsten.

Although the present invention has been described in connection with specific examples and embodiments, it will be recognized by those skilled in the art the variations and modifications of which the present invention is capable without departing from the broad scope of the present invention as represented by the appended claims.

It is to be understood by those skilled in the art that the porous metal products produced by the methods of the current invention will find a wide variety of commercial application and in particular will find application in air and gas filters, catalyst supports, catalytic converters, flame arrestors, electro-chemical cathodes, biomaterial applications, lightweight structures, sound dampeners and diesel particulate traps, as well as waste water particulate filters and/or traps.

CLAIMS

1. A method of forming a porous metal comprising the steps of:

a) selecting an organic reticulated precursor material having a predetermined cell size;

b) preparing a slurry of binder and metal powder;

c) impregnating said organic reticulated precursor material with said slurry;

d) curing the impregnated organic material;

e) heating the cured impregnated organic material and the slurry, retaining the shape of the original organic structure;

f) heating the remaining material structure to remove the presence of any carbonaceous material;

g) heating the remaining structure to sinter said structure.

2. A method of forming a porous copper metal comprising the steps of:

a) selecting an organic reticulated precursor material having a predetermined cell size;

b) preparing a slurry of binder and metal powder, said binder selected from the family of phenolic or PVA binders;

c) impregnating said organic reticulated precursor material with said slurry;

d) curing the impregnated organic material by heating in air at 250 to 350 Degrees F for 0.5 to 3.0 hrs;

e) heating the cured impregnated organic material and the slurry eliminating the organic retriculated precursor material while retaining the shape of the original organic structure;

f) heating the remaining material structure to remove the presence of any carbonaceous material;

g) heating the remaining structure at 1550 to 1800 Degrees F for 0.5 to 1.0 hrs. in hydrogen to sinter said structure.

3. The method of Claim 2 wherein the organic reticulated precursor material is eliminated by heating the cured structure to 1200 Degrees F to 1600 Degrees F for 2 to 3 hours in 20 to 30 scfh of any inert or reducing atmosphere.

4. The method of Claim 2 wherein the organic retriculated precursor material is eliminated by heating the cured structure to 1700 Degrees F to 1900 Degrees F in air for 1 to 3 hours.

5. The method of Claim 2 wherein the decarburization is completed by processing water through a retort at 0.5 to 1.0 gallons per hr. at 1200 to 1600 Degrees F.

6. The method of Claim 2 wherein the decarburization is completed by heating the cured organic material and slurry in air from 1100 Degrees F to 1900 Degrees F for 1 to 3 hours.

7. The method of Claim 2 wherein the porous material produced is sintered at 1550 Degrees F to 1800 Degrees F for 0.5 to 1.0 hrs. in hydrogen.

8. The method of Claim 2 wherein the organic retriculated precursor material is impregnated by coating the foam with binder and sprinkling or spraying dry metal powder on and into the foam material.

9. The method of Claim 2 wherein the organic retriculated precursor material is impregnated by applying binder and dry metal powder using a fluidized bed means.

10. The method of Claim 2 wherein the slurry of binder and metal powder is in the proportion of 2 to 4 parts binder to 6 to 8 parts copper oxide or copper powder.

11. A method of forming a porous nickel metal comprising the steps of:

a) selecting an organic reticulated precursor material having a predetermined cell size;

b) preparing a slurry of binder and metal powder, said binder selected from the family of phenolic or PVA binders;

c) impregnating said organic reticulated precursor material with said slurry;

d) curing the impregnated organic material by heating in air at 250 to 350 Degrees F for 0.5 to 3.0 hrs;

e) heating the cured impregnated organic material and the slurry eliminating the organic retriculated precursor material while retaining the shape of the original organic structure;

f) heating the remaining material structure to remove the presence of any carbonaceous material;

g) heating the remaining structure at 1800 to 2300 Degrees F for 0.5 to 1.0 hrs. in hydrogen to sinter said structure.

12. The method of Claim 11 wherein the organic reticulated precursor material is eliminated by heating the cured structure to 1200 Degrees F to 1600 Degrees F for 2 to 3 hours in 20 to 30 scfh of any inert or reducing atmosphere.

13. The method of Claim 11 wherein the organic retriculated precursor material is eliminated by heating the cured structure to 1700 Degrees F to 1900 Degrees F in air for 1 to 3 hours.

14. The method of Claim 11 wherein the decarburization is completed by processing water through a retort at 0.5 to 1.0 gallons per hr. at 1200 to 1600 Degrees F.

15. The method of Claim 11 wherein the decarburization is completed by heating the cured organic material and slurry in air from 1100 Degrees F to 2800 Degrees F for 1 to 3 hours.

16. The method of Claim 11 wherein the organic retriculated precursor material is impregnated by coating the foam with binder and sprinkling or spraying dry metal powder on and into the foam material.

17. The method of Claim 11 wherein the organic retriculated precursor material is impregnated by applying binder and dry metal powder using a fluidized bed means.

18. The method of Claim 11 wherein the slurry of binder and metal powder is in the proportion of 2 to 4 parts binder to 6 to 8 parts copper oxide or copper powder.

19. A method of forming porous nickel alloys and iron alloys containing high chromium metal comprising the steps of:

a) selecting an organic reticulated precursor material having a predetermined cell size;

b) preparing a slurry of binder and metal powder, said binder selected from the family of phenolic or PVA binders;

c) impregnating said organic reticulated precursor material with said slurry;

d) curing the impregnated organic material by heating at 250 to 350 Degrees F for 0.5 to 3.0 hrs;

e) heating the cured impregnated organic material and the slurry to 1600 to 2000 Degrees F for 2 to 3 hrs in a vacuum atmosphere with a partial pressure of argon in the range of 2500 to 3500 microns, burning off the foam structure while retaining the shape of the original organic structure;

f) heating the remaining material structure to remove the presence of any carbonaceous material at 900 to 1200 Degrees F for 3 to 12 hrs.;

g) heating the remaining structure at 2200 to 2500 Degrees F for 0.5 to 1.0 hrs. in vacuum with a partial pressure of argon in the range of 2500 to 3500 microns to sinter said structure.

20. The method of Claim 19 wherein the organic reticulated precursor material is impregnated by coating the foam with binder and sprinkling or spraying the metal powder on and into the foam material.

21. The method of Claim 19 wherein the organic retriculated precursor material is impregnated by coating the foam with binder and sprinkling or spraying dry metal powder on and into the foam material.

22. The method of Claim 19 wherein the organic retriculated precursor material is impregnated by applying binder and dry metal powder using a fluidized bed means.

23. The method of Claim 19 wherein the slurry of binder and metal powder is in the proportion of 2 to 4 parts binder to 6 to 8 parts copper oxide or copper powder.

24. A method of forming Alpha 4® porous material comprising the steps of:

a) selecting an organic reticulated precursor material having a predetermined cell size;

b) preparing a slurry of binder and metal powder, said binder selected from the family of phenolic or PVA binders;

c) impregnating said organic reticulated precursor material with said slurry;

d) curing the impregnated organic material by heating at 250 to 350 Degrees F for 0.5 to 3.0 hrs;

e) heating the cured impregnated organic material and the slurry to 2300 Degrees F to 2450 Degrees F for 0.5 to 2.0 hrs. in vacuum with a partial pressure of 2500 to 3500 microns of nitrogen or argon completing foam burnoff and sinter.

25. The method of Claim 24 wherein the organic retriculated precursor material is impregnated by coating the foam with binder and sprinkling or spraying dry metal powder on and into the foam material.

26. The method of Claim 24 wherein the organic retriculated precursor material is impregnated by applying binder and dry metal powder using a fluidized bed means.

27. The method of Claim 24 wherein the slurry of binder and metal powder is in the proportion of 2 to 4 parts binder to 6 to 8 parts copper oxide or copper powder.

28. The method of Claim 24 wherein the cell size developed is 50 ppi or greater.

29. The method of Claim 24 wherein the porous metal developed is selected from the group consisting of chromium, columbium, iron aluminide, nichel aluminide, titanium aluminide, aluminum in solution and rare earths in solution;

30. A method of forming porous titanium and titanium alloys comprising the steps of:

a) selecting an organic reticulated precursor material having a predetermined cell size;

b) preparing a slurry of binder and metal powder, said binder selected from the family of phenolic or PVA binders;

c) impregnating said organic reticulated precursor material with said slurry;

d) curing the impregnated organic material by heating at 250 to 350 Degrees F for 0.5 to 3.0 hrs;

e) heating the cured impregnated organic material and the slurry to 2200 to 2700 Degrees F for 0.5 to 1.0 hrs in a vacuum atmosphere with a partial pressure of 2500 to 3500 microns of argon burning off the foam structure while retaining the shape of the original organic structure;

31. The method of Claim 30 wherein the organic retriculated precursor material is impregnated by coating the foam with binder and sprinkling or spraying dry metal powder on and into the foam material.

32. The method of Claim 30 wherein the organic retriculated precursor material is impregnated by applying binder and dry metal powder using a fluidized bed means.

33. The method of Claim 30 wherein the slurry of binder and metal powder is in the proportion of 2 to 4 parts binder to 6 to 8 parts copper oxide or copper powder.

34. The method of Claim 30 wherein the cell size develops is 50 ppi or greater.

35. A method of forming porous precious metals comprising the steps of:

a) selecting an organic reticulated precursor material having a predetermined cell size;

b) preparing a slurry of binder and metal powder, said binder selected from the family of phenolic or PVA binders;

c) heating the organic retriculated precursor material in air at 2700 Degrees F to 3000 Degrees F for 0.5 to 2 hrs.

36. The method of Claim 35 wherein the organic retriculated precursor material is impregnated by coating the foam with binder and sprinkling or spraying dry metal powder on and into the foam material.

37. The method of Claim 35 wherein the organic retriculated precursor material is impregnated by applying binder and dry metal powder using a fluidized bed means.

38. The method of Claim 35 wherein the slurry of binder and metal powder is in the proportion of 2 to 4 parts binder to 6 to 8 parts copper oxide or copper powder.

39. A method of forming porous metals and alloys from the group of refractory metals and alloys consisting of molybdenum, tantalum, columbian and tungsten comprising the steps of:

a) selecting an organic reticulated precursor material having a predetermined cell size;

b) preparing a slurry of binder and metal powder, said binder selected from the family of phenolic or PVA binders;

c) heating the impregnated foam structure to 1600 Degrees F to 2000 Degrees F in nitrogen;

d) heating at 1600 Degrees F to 2000 Degrees F in an atmosphere of 20 to 30 scfh of hydrogen with 0.1 to 0.25 gallons of water for 6 to 10 hours;

e) heating in a vacuum furnace to 2800 Degrees F to 3200 Degrees F for 0.5 to 2 hours.

40. The method of Claim 39 wherein the organic retriculated precursor material is impregnated by coating the foam with binder and sprinkling or spraying dry metal powder on and into the foam material.

41. The method of Claim 39 wherein the organic retriculated precursor material is impregnated by applying binder and dry metal powder using a fluidized bed means.

42. The method of Claim 39 wherein the slurry of binder and metal powder is in the proportion of 2 to 4 parts binder to 6 to 8 parts copper oxide or copper powder.

PREPARATION OF SLURRY
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FOAM IMPREGNATION
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CURING FOAM STRUCTURE
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BURN OFF FOAM STRUCTURE
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\|/
DECARBURIZATION
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\|/
SINTERING

FIG 1

FOAM COATING
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METAL POWDER APPLICATION
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\|/
CURING FOAM STRUCTURE
|
\|/
BURN OFF FOAM STRUCTURE
|
\|/
SINTERING

FIG 2

FIG 3

INTERNATIONAL SEARCH REPORT

Intern al Application No
PCT/US 97/02561

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B22F3/11

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B22F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 95 26844 A (HITACHI CHEMICAL CO LTD ;HIRATSUKA HATSUE & HF (JP); KAMIGATA YASU) 12 October 1995 see abstract ---	1-42
Y	GB 963 885 A (GENERAL ELECTRIC COMPANY) 15 July 1964 see the whole document ---	1-42
A	US 3 313 621 A (L.H.MOTT) 11 April 1967 see column 1, line 50 - column 2, line 65; claim 6 ---	1-10
A	EP 0 099 337 A (ELTECH SYST LTD) 25 January 1984 see page 20, line 10 - line 30 --- -/--	1,2,11, 19,24, 30,39

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

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Date of the actual completion of the international search	Date of mailing of the international search report
17 July 1997	25.07.97

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Schruers, H

INTERNATIONAL SEARCH REPORT

Interr. ul Application No
PCT/US 97/02561

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Information on patent family members

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